

# Surface spectroscopy of nano-scale reactions in aqueous solution

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## INTRODUCTION

The rate of oxidation of dissolved Mn(II) by oxygen is enhanced in the presence of catalytic surfaces. Surfaces of iron oxides such as Goethite ( $\alpha$ -FeOOH), Lepidocrocite ( $\gamma$ -FeOOH), and Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) can increase the rate of Mn(II) oxidation over the initial homogeneous solution rate by orders of magnitude [1, 2]. These reactions are further complicated by the observation that initially formed reaction products are metastable and depend strongly on both the bulk reaction conditions such as temperature, concentration of Mn(II), pH-value, presence of dominant anions [3-5], and interfacial reaction conditions existing at the catalytic surfaces. The activities of reactants and products and especially the thermodynamic properties of Mn(III) species at such surfaces are not known and are not readily measurable [4]. In addition, initially formed Mn-oxides or hydroxides may autocatalytically enhance reaction rates [6]. A contribution from autocatalytic oxidation of Mn(II) has been hypothesized for the formation of Mn-micronodules in lake sediments [7] and the occurrence of Mn-biominerals formed by spores of a marine bacillus *SG-1* [e.g. 8, 9]. It is therefore quite natural that details on the identity of reaction products vary a lot in the literature.

Traditionally, two different approaches have been utilized to study Mn(II) oxidation at mineral surfaces: a macroscopic approach using wet chemistry data and surface complexation models [10], and a microscopic approach using Scanning Force Microscopy and surface spectroscopic techniques [11]. Junta-Rosso et al. [12] have also tried to link both microscopic and macroscopic data to develop rate expressions that are consistent with both approaches. The microscopic as well as surface spectroscopic techniques applied in those studies suffer from transfer of wet samples into high vacuum, the effect of which has not yet been studied systematically. We have used Scanning Transmission X-ray Spectromicroscopy (STXM) to characterize products formed during the heterogeneous oxidation of Mn(II) by dissolved oxygen on fully hydrated single nano-sized particles of catalytically active iron oxides.

## MATERIALS AND METHODS

Aliquots of powdered iron oxides (Goethite, Lepidocrocite, and Hematite) equivalent to 25 m<sup>2</sup>L<sup>-1</sup> were each suspended in 10 mM HEPES solution (pH 7.8, 50 mM NaCl) and equilibrated for 24 h. Characteristics of the used iron oxides are given elsewhere [13]. These suspensions were kept open to atmosphere on a multi stirring plate and were repeatedly spiked with aliquots from a 55 mM MnCl<sub>2</sub> stock solution. Time intervals between sequential addition of Mn(II) were chosen long enough to keep the concentration of dissolved Mn(II) below 0.3 mM.

Two sets of samples were withdrawn for STXM measurements: (a) after 96 d of reaction time and a total Mn(II)-dosage of 244  $\mu$ M, and (b) after 129 d of reaction time and a total Mn(II)-dosage of 1.26 mM. All X-ray absorption measurements were done at the Advanced Light Source (Lawrence Berkeley National Laboratory) on beam line 7.0.1. Sample preparation and

technical specifications of an upgrade version of STXM are given elsewhere [14, 15]. Data analysis and spectral interpretation using XANES of reference compounds are detailed in [16].

## RESULTS AND DISCUSSION

STXM of the first set of samples withdrawn after 96 days and a total Mn(II) dose of 244  $\mu\text{M}$ , did not result in detectable amounts of Mn on the iron oxide particles. Obviously, the mass of adsorbed Mn(II) and/or oxidation products present on the particles were below the detection limit of the instrument. Figure 1 shows single needles of Goethite after 129 d of incubation imaged at the Fe absorption maximum and the corresponding XANES of the Mn-edge. The spectrum could be fitted by a linear combination of spectra of single valent Mn(II) and Mn(III)-reference models. Fits did not improve by including any Mn(IV)-component.

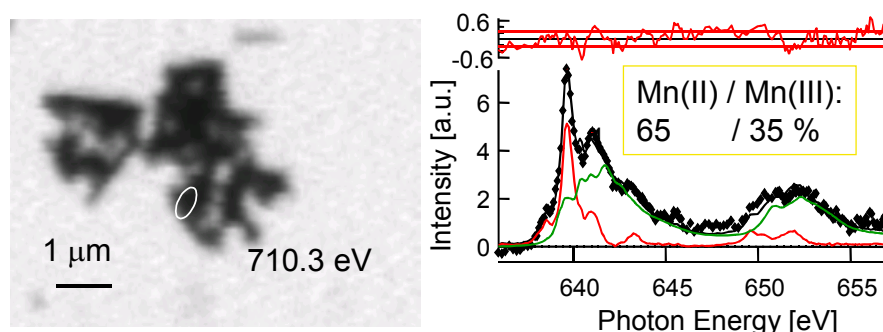


Figure 1. Image of single needles of Goethite (left) and XANES (◆) at the Mn-edge extracted from the area labeled on the image. The XANES is fitted to a linear combination of spectra of single valent reference compounds (red:  $\text{MnSO}_4$ , green:  $\gamma\text{-MnOOH}$ ). Quantitative results are given in mass % of each charge component and residuals are plotted with the horizontal lines indicating  $\pm$  one standard deviation.

Under the experimental conditions used, the iron oxide catalyzed oxidation of Mn(II) led to a mixed valent Mn(II)/Mn(III)-species (most likely Hausmannite [4,5]), the stoichiometric ratio of which might be superimposed by specific adsorption of  $\text{Mn}^{2+}$  from solution. Control experiments under anoxic conditions are necessary to decide whether the high Mn(II)-content is due to adsorption of  $\text{Mn}^{2+}$  onto iron oxide surfaces or incorporation into oxidation products. Within the time frame of our experiment, we can rule out disproportionation of initial Mn(III)-species, although this reaction is thermodynamically favorable under our bulk reaction conditions. We hypothesize that reaction conditions at the iron oxide interfaces can stabilize Mn(III).

Comparing the mass fraction of Mn(III) on all three iron oxides, the order is  $\alpha\text{-FeOOH} \gg \alpha\text{-Fe}_2\text{O}_3 > \gamma\text{-FeOOH}$ , which does not correlate with the amount of specific sites for cation sorption on those oxides. The observed order, however, does correlate with the order of catalytic activities observed during reductive dehalogenation of polyhalogenated methanes by Fe(II) sorbed to exactly the same iron oxides [13]. We conclude that unknown steric/electronic properties of the iron oxide substrates might be involved as controlling factors in lowering the redox potential of transition metal cations sorbed to such surfaces.

## ACKNOWLEDGMENTS

Thanks to Sirine Fakra, Rick Steele and Tony Warwick for providing such a wonderful instrument. Adam Hitchcock and Eli Rotenberg provided software for data analysis.

## REFERENCES

- [1] Diem, D.; Stumm, W. *Geoch. et Cosmoch. Acta* 1984, 48,1571-1573.
- [2] Sung, W.; Morgan, J.J. *Geoch. et Cosmoch. Acta* 1981, 45,2377-2383.
- [3] Hem, J.D. *Geoch. et Cosmoch. Acta* 1981, 45,1369-1374.
- [4] Hem, J.D.; Lind, C.J. *Geoch. et Cosmoch. Acta* 1983, 47, 2037-2046.
- [5] Murray, J.W.; Dillard, J.G.; Giovanoli, R.; Moers, H.; Stumm, W. *Geoch. et Cosmoch. Acta* 1985, 49,463-470.
- [6] Murray, J.W. *Geoch. et Cosmoch. Acta* 1975, 39,505-519.
- [7] Murray, L.W.; Balistrieri, L.S.; Paul, B. *Geoch. et Cosmoch. Acta* 1984, 48,1237-1247.
- [8] Nealson, K.H.; Tebo, B.M. *Adv. Appl. Microbiol.* 1988, 33,279-318.
- [9] Mandernack, K.W.; Post, J.; Tebo, B.M. *Geoch. et Cosmoch. Acta* 1995, 59,4393-4408.
- [10] Davies, S.H.R.; Morgan, J.J. *J. Colloid Interface Sci.* 1989, 129,63-77.
- [11] Junta, J.L.; Hochella Jr., M.F. *Geochim. Cosmochim. Acta* 1994, 58,4985-4999.
- [12] Junta-Rosso, J.L.; Hochella Jr., M.F.; Rimstidt, J.D. *Geoch. et Cosmoch. Acta* 1997, 61,149-159.
- [13] Pecher, K.; Haderlein, S. B.; Schwarzenbach, R. P. *Environ. Sci. Technol.* 2001 accepted.
- [14] <http://www-esg.lbl.gov/Stxm/>
- [15] Pecher, K.; Kneedler, E.; Rothe, J.; Meigs, G.; Warwick, T.; Nealson, K.; Tonner, B. In: *X-ray Microscopy (XRM'99)*; AIP Conference Proceedings 507, W. Meyer-Ilse, T. Warwick, D. Attwood (Eds.); Berkeley, 2000; p 291-300.
- [16] Pecher, K.; McCubbery, D.; Kneedler, E.; Rothe, J.; Bargar, J.; Meigs, G.; Cox, L., Nealson, K.; Tonner, B. submitted to *Geoch. et Cosmoch. Acta* 2001.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. This work was supported by grants from DOE Division of Materials Sciences FG02-98ER45688 and DOE NABIR FG02-97ER62474.

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